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Magnesium Carbonate - A Recycled Coagulant from Water Treatment. Capsule Report

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This Capsule Report explains the new magnesium recycle coagulation system for water treatment, which is based on a combination of water softening and conventional coagulation techniques which can be applied to all types of water. This system offers an alternative approach to chemical sludge handling as well as providing for reuse of the chemicals.

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CAPSULE REPORT

MAGNESIUM CARBONATE - A RECYCLED COAGULANT FOR WATER TREATMENT

PREPARED BY U.S. ENVIRONMENTAL PROTECTION AGENCY

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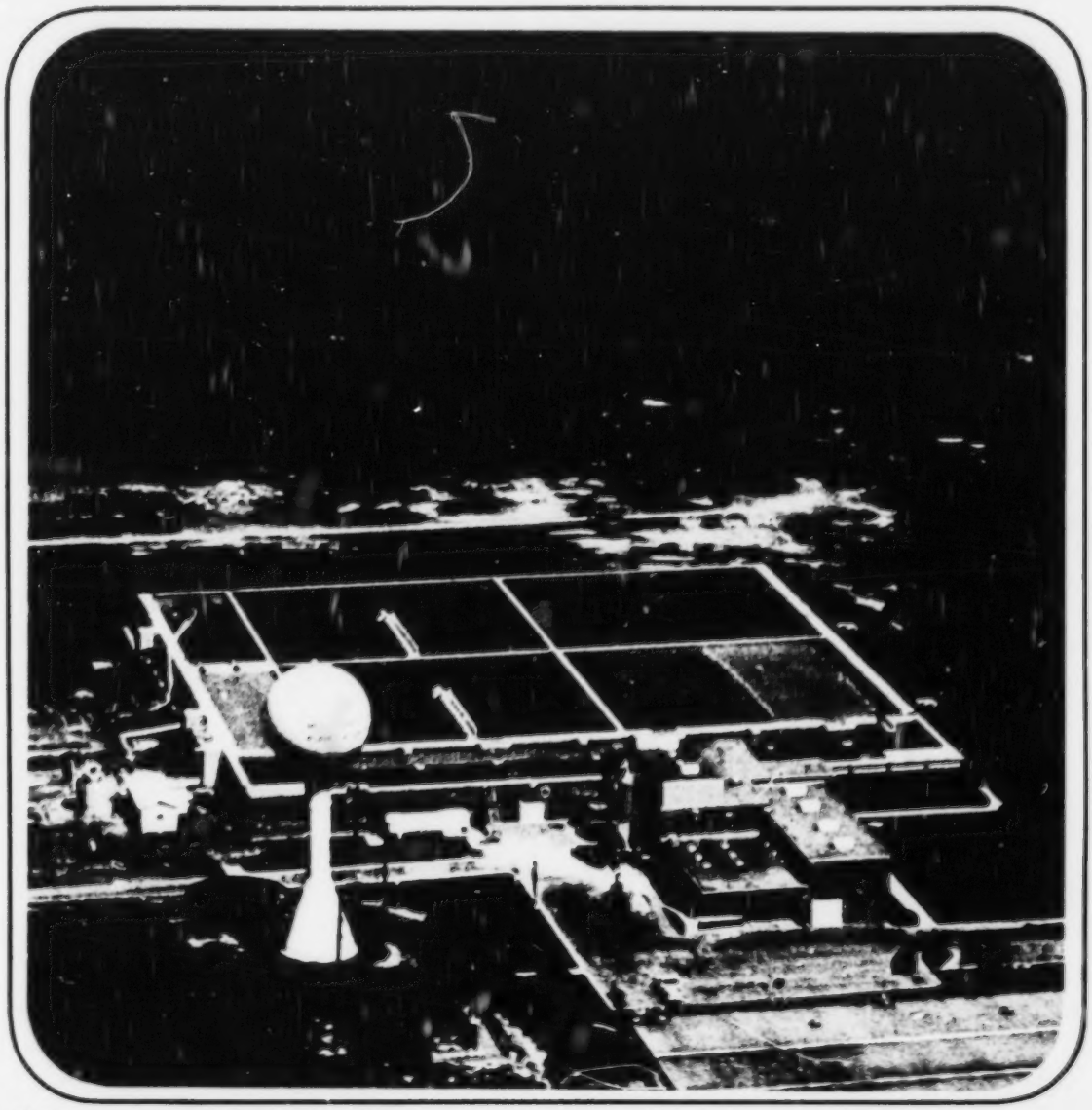


Montgomery Water Treatment Plant

1. THE SIGNIFICANCE

Approximately 1 million tons per year of dry solids are produced from an estimated 3,600 water treatment plants practicing coagulation throughout the country. Of these, less than 5 percent receive treatment of any kind before return to the water course. Wastes from water treatment plants are today recognized as a significant pollution problem.

Lime-soda softening plants produce considerably more solids per million gallons of water treated than are produced in a typical chemical coagulation plant. It has been estimated that from 0.45 to 0.66 acre-foot per year of 50 percent solids sludge are produced for each 100 ppm of hardness removed from 1 mgd of water. The sludge produced in water softening plants is primarily calcium carbonate, which can be concentrated and dewatered more readily than predominately metal hydroxide sludges.

A number of devices are available for dewatering water plant sludges, although costs have been found to be high. Dewatering alone still leaves a solid waste management problem. To date, lime recovery has been found practical on only relatively pure calcium carbonate sludges.

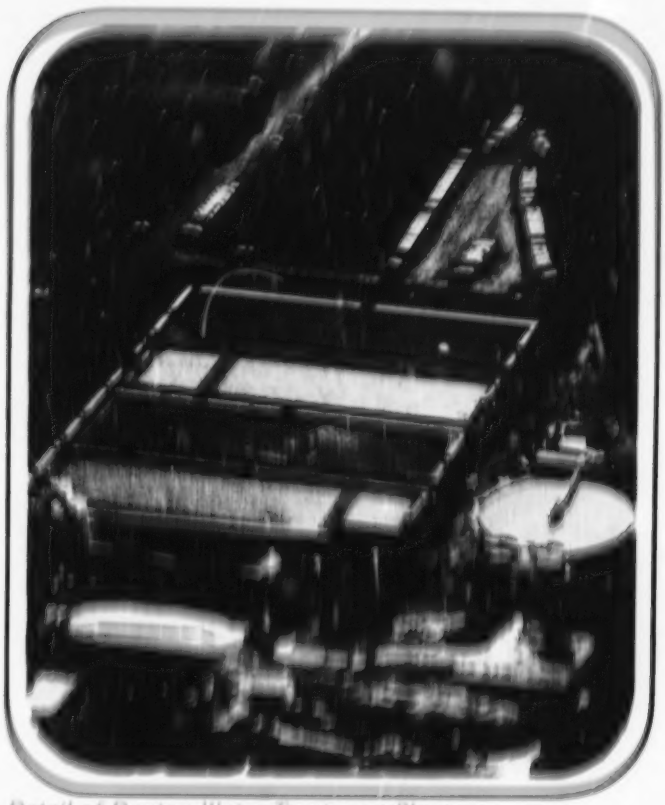
The new magnesium recycle coagulation system is based on a combination of water softening and conventional coagulation techniques which can be applied to all types of water. This system offers an alternative approach to chemical sludge handling as well as providing for reuse of the chemicals. The development of this new process has been supported by grants from the U. S. Environmental Protection Agency; the Montgomery, Alabama, Water and Sanitary Sewer Board; the city of Melbourne, Florida; and the American Water Works Association Research Foundation. In addition, the city of Dayton, Ohio, has provided additional support.

The photograph on the opposite page is an aerial view of the Montgomery Water Treatment Plant showing the parallel operation with two coagulants – $MgCO_3$ (foreground) and alum.

The major areas of significance offered by this new technology are:

- Sludge discharges are reduced or completely eliminated and the sludge water, recovered as treated water, is an important saving for large plants.
- The water is treated primarily by three chemicals (lime, carbon dioxide, and magnesium carbonate), which are recovered or recycled.
- Significant cost savings are realized for most applications, particularly when sludge disposal costs are considered.
- Floc characteristics allow significant increases in clarifier loading rates, increasing the clarifier capacity of many plants.
- The treated water produced is of high chemical and bacteriological quality. Soft waters are made chemically stable, hard waters are softened, and the high pH of the process provides added assurance of disinfection. In addition, many heavy metals are removed in the water treatment process.
- The process can be readily adapted to the current potable water filtration plant using chemical coagulation, and to conventional lime-soda softening plants.

2. THE NEW PROCESS



Detail of Dayton Water Treatment Plant

In this new technology, developed by Dr. A. P. Black, the primary treatment chemicals (lime, carbon dioxide, and magnesium carbonate) are recovered and recycled.

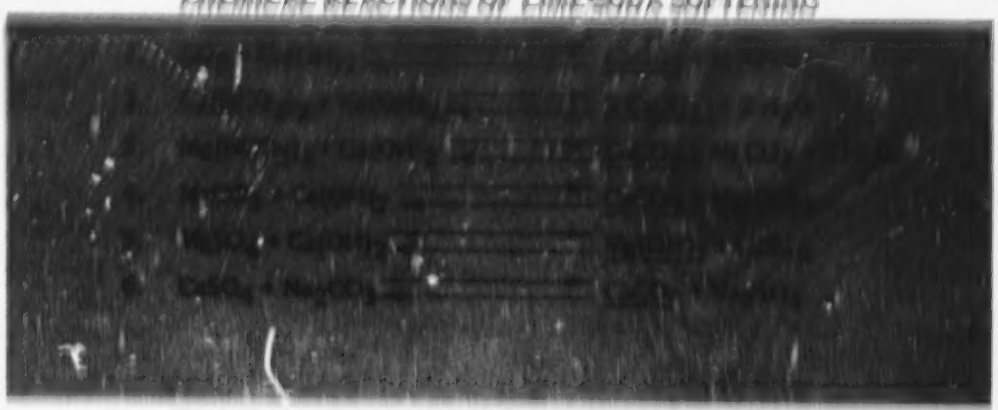
The process development began in 1957 at the Dayton, Ohio water treatment plant (front cover), where a hard, clear, high magnesium water is softened by the lime-soda process, involving the first six reactions shown in Table 1. Sludge components are underlined. Approximately 300 tons of sludge per day, dry basis, are produced, containing 12 percent magnesium hydroxide with the remainder primarily calcium carbonate.

For all types of water, magnesium carbonate is precipitated as magnesium hydroxide, which then becomes the active coagulant. The resulting sludge is composed of $CaCO_3$, $Mg(OH)_2$ and, in the case of turbid waters, the turbidity removed from the raw water. Reactions 7, 8a, and 8b describe how the sludge is carbonated by injecting CO_2 gas which selectively dissolves the $Mg(OH)_2$. The carbonated sludge is then filtered with the magnesium being recovered as soluble magnesium bicarbonate in the filtrate, which is recycled to the point of addition of chemicals to the raw water, reprecipitated as $Mg(OH)_2$ (Eqs. 3 and 4, Table 1), and a new treatment cycle begun. The filter cake now contains $CaCO_3$ and the raw water turbidity. In large plants, it is possible to reduce the waste solids even further by slurrying the filter cake and separating the raw water turbidity from the $CaCO_3$ by flotation. The purified $CaCO_3$ is dewatered and recalcined as high quality quicklime as shown in reaction 9. The stack gases from the recalcining operation then provide the CO_2 gas for carbonating the sludge for magnesium recovery and to recarbonate the water in the treatment plant. When this latter lime recovery step is practiced, the waste solids are reduced to only those which constitute raw water turbidity.

If magnesium is to be recovered, the magnesium bicarbonate solution, clarified by either settling or filtration, passes to a heat exchange unit where it is warmed to 35° C - 45° C after which it is aerated by compressed air in a mechanically mixed basin. The $MgCO_3 \cdot 3H_2O$ (Eq. 10, Table 1) precipitation is complete in about 90 minutes and the resulting product is vacuum filtered, dried, and sold.

CHEMICAL SUMMARY OF THE NEW PROCESS

CHEMICAL REACTIONS OF LIME-SODA SOFTENING



CHEMICAL REACTIONS FOR SLUDGE CARBONATION

CHEMICAL REACTION FOR CALCINATION

CHEMICAL REACTION FOR PRODUCT RECOVERY

Table I

3. THE OLD PROCESS VS. THE NEW

COMPARISON OF CONVENTIONAL COAGULANTS WITH MAGNESIUM CARBONATE

CHARACTERISTICS	CONVENTIONAL	MAGNESIUM CARBONATE
pH of optimum coagulation	Usually in the range pH 5.2 through 5.7 for organic color, somewhat higher for turbidity.	pH 11.3 when magnesium recovery is to be made. For magnesium recycle only pH 10.9 through 11.1, but may be pH 11.3.
Flocculation	Hydrolysis product. Forms slowly, more so at low temperatures. Sensitive to high velocity gradients.	Large, dense, the $Mg(OH)_2$ coagulant weighed down by the coprecipitated $CaCO_3$. Less sensitive to temperature changes.
Settling	Settles slowly. Clarifier flow rate less than 0.75 gal/ft^2/min. Sensitive to convection currents.	Settles rapidly. Clarity of settled water at Montgomery dramatically better than alum. Upflow rate in Melbourne's clarifiers double that of alum.
Sludge	Gelatinous sludge normally 1 to 2 percent solids. Thickens to only about 6 percent solids.	Primary sludge 3 to 5 percent solids. Carbonated sludge thickens to 40 to 50 percent solids.
Sludge water	Rarely, if ever, recovered.	About 90 percent recovered, recycled and added to plant effluent as treated water. This represents a significant saving for large plants.

CHARACTERISTICS	CONVENTIONAL	MAGNESIUM CARBONATE
Finished water	Low total hardness. Low alkalinity, usually in range 10 to 25 ppm. Not possible to stabilize by pH adjustment. "Red water" problems common.	Somewhat higher total hardness. Alkalinity 35 to 50 ppm. May be stabilized by pH adjustment to produce non-corrosive effluent. Total hardness depends upon noncarbonate hardness present.
Filtration	Fine gelatinous floc may reduce length of filter runs.	$CaCO_3$ turbidity of stablized water does not reduce filter runs. Filter runs at Montgomery consistently longer than with alum. Filtered turbidities lower.
Adaptability to existing plants	Usually designed for the use of alum or a ferric salt.	Readily adaptable without plant changes in most areas. When coagulation is at pH 11.3, two-stage carbonation used; stage 1 to pH 10 3; stage 2 to final pH of water.
Bacteriological quality of treated water	Dependent upon quality of raw water and type of residual carried.	High pH of coagulation provides complete disinfection and should eliminate pre-chlorination.

4. AREAS OF APPLICATION

There are three general applications of this new technology in water treatment dependent upon the quantity and character of the raw water treated.

These applications are:

(1) Soft, Turbid and/or Colored Waters

Figure 1 shows magnesium being used as the coagulant, with the recycle of magnesium bicarbonate and sludge dewatering as an integral part of the process. The Montgomery study demonstrated this application to be successful.

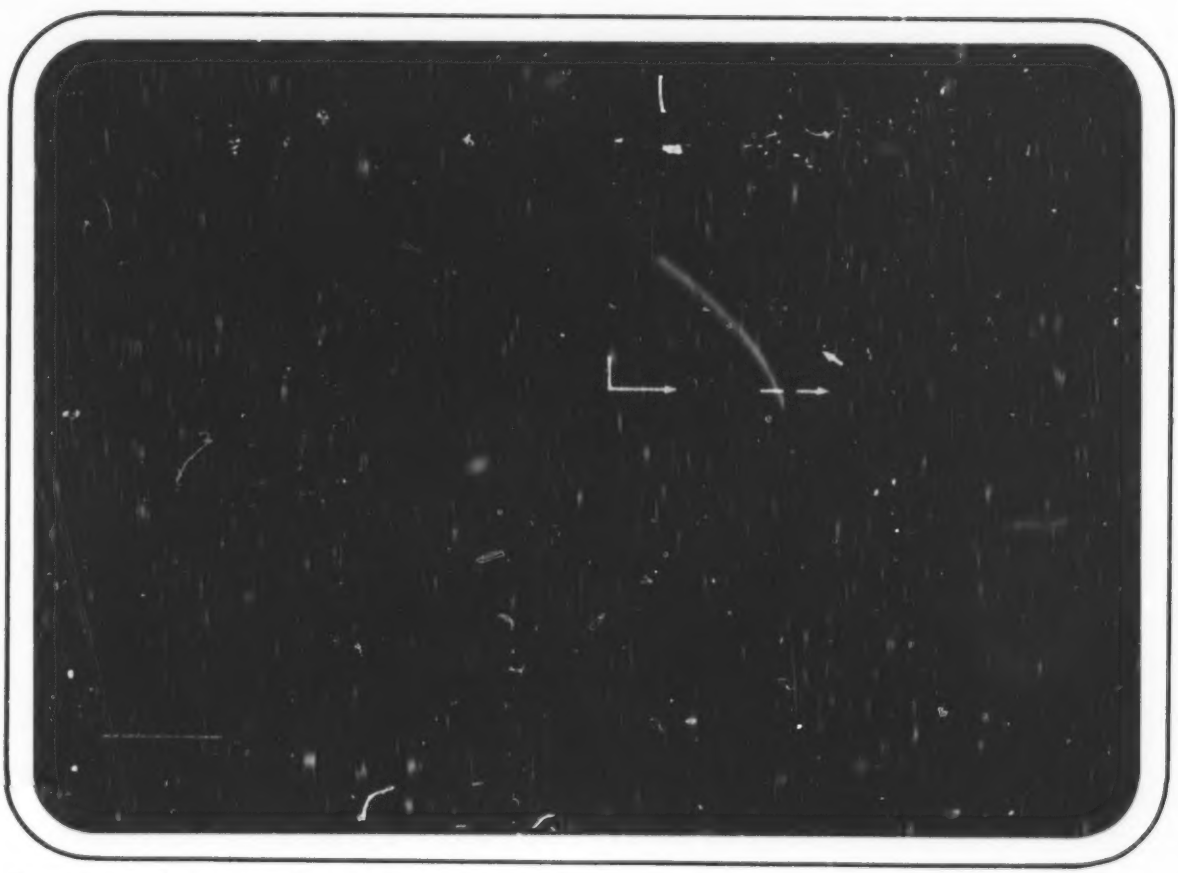


Figure 1. Soft, turbid and/or colored waters

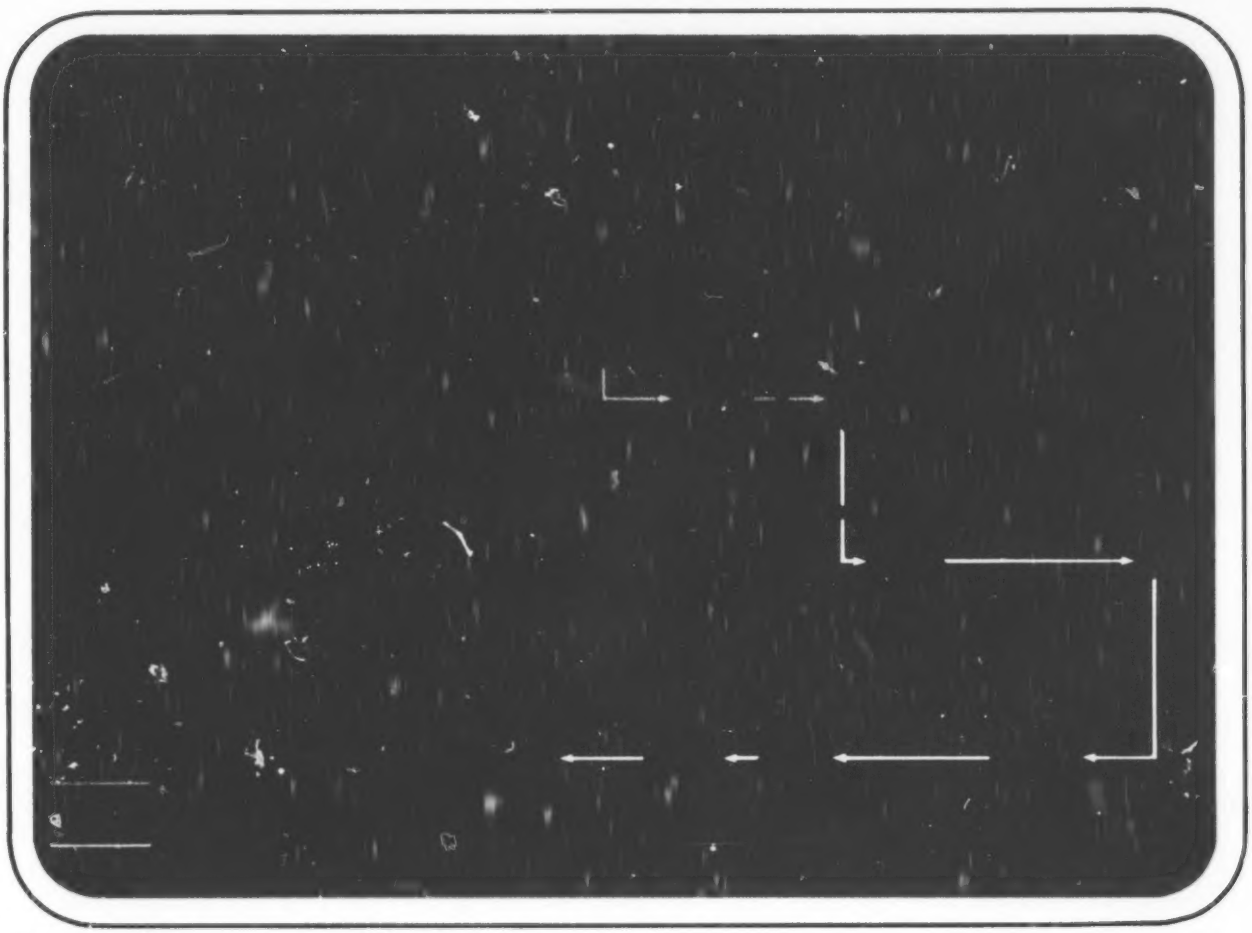


Figure 2. Moderately hard, turbid and/or colored waters

(2) Moderately Hard, Turbid and/or Colored Waters

Figure 2 demonstrates magnesium being used as a recycled coagulant, but lime recovery is also included. In some cases, the flotation step will not be required due to low suspended solids in the raw water. Carbon dioxide produced in lime recovery is used for softened water stabilization and carbonation of the sludge.

(3) **Hard, High Magnesium, Clear or Turbid Waters**

In this application, both calcium and magnesium are recovered. Part of the lime is recycled and the remainder is sold. In addition, the magnesium carbonate is sold. Figure 3 illustrates the unit operations necessary for this application when treating a hard (125 to 300 mg/l), turbid, high magnesium (10 to 30 mg/l) water.

There are a number of major cities which fall into this category. Dayton, Ohio, where a clear, high magnesium, hard water is softened, is a good illustration of an application in this category. Lime recovery is now practiced, with magnesium recovery soon to be added.

The primary emphasis of each of these applications is the elimination of sludge disposal problems by the recycle or recovery of the three water treatment chemicals used (lime, carbon dioxide, and magnesium). This technology also has potential for the treatment of municipal and industrial wastewater.

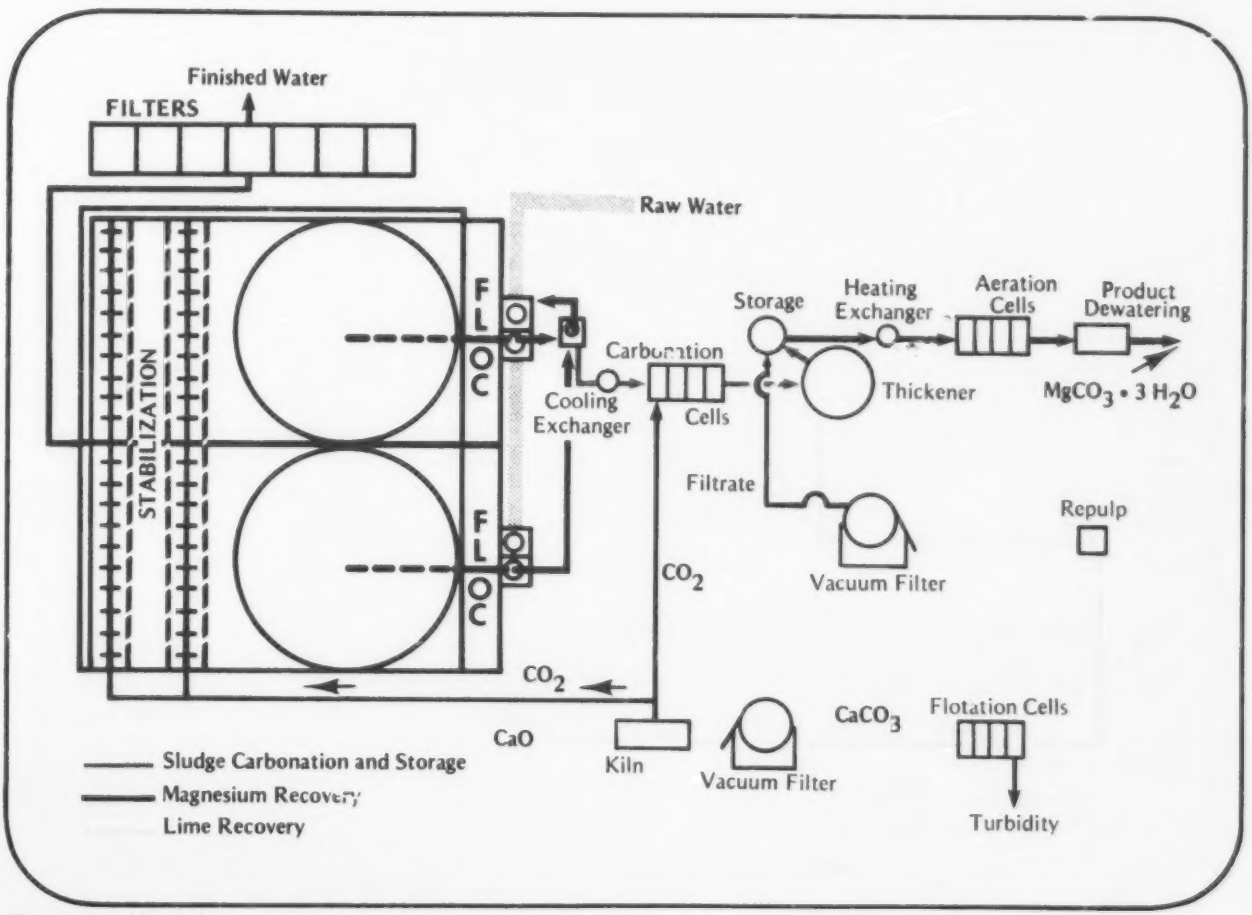


Figure 3. Hard, high magnesium, clear or turbid waters

5. THE ECONOMICS

Equalizing sludge lagoon at Dayton

The economics of the new process are most favorable in the case of hard, high magnesium waters where recalcination is practiced. This is because all of the three essential chemicals are recovered, recycled or sold.

The economic benefits of the new technology can be substantial. During the 16-year period 1958 through 1973, Dayton produced 505,462 tons of high quality lime valued at $9 million. Approximately 100,000 tons of lime valued at more than $1 million has been produced and sold to other during this period.

Chemical treatment costs are substantially reduced in several ways. The coagulant used by all water treatment plants, alum or an iron salt, is replaced by the magnesium present in the raw water. The recovery of high quality quicklime by recalcining reduces lime costs by about 50 percent and provides, at no cost, sufficient carbon dioxide from the kiln stack gas to carbonate the treated water. Carbon dioxide is also used to recover or recycle the magnesium in the sludge. Sludge water is recycled to the plant and recovered.

The following additional savings will be realized:

a. Sale of excess lime produced.
b. Sale of magnesium produced.
c. Cost of an alternate method of sludge disposal.

Other potential savings include:

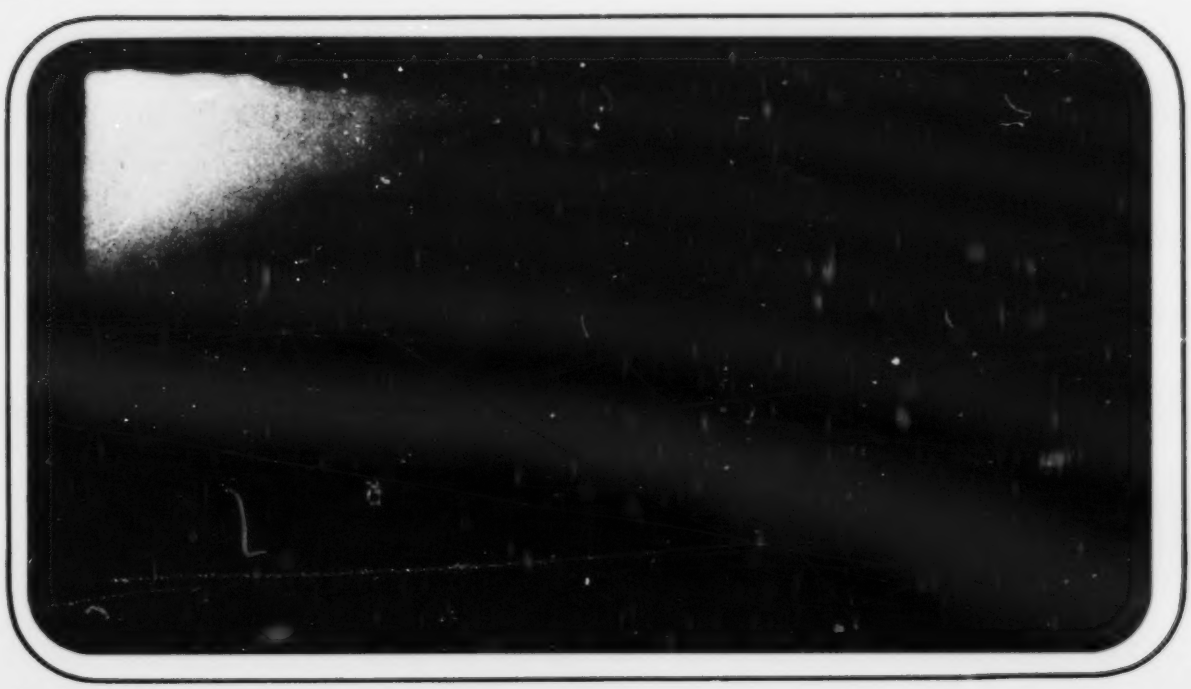
a. The possibility of reducing the amount of chlorine used for pre-chlorination or perhaps eliminating it entirely.
b. Production of a soft, stable treated water.
c. Potential significant increase in treatment capacity with minor plant modification.

In the case of soft, turbid and/or colored waters, plant size and daily lime consumption are the key factors determining the cost of treatment. If daily lime usage is sufficient to justify recalcination of sludge, treatment costs should be as low or lower than present treatment costs. However, without recalcination, treatment costs will probably be higher because the kiln provides both lime and carbon dioxide. In such cases, the cost of sludge disposal becomes the most important determining factor.

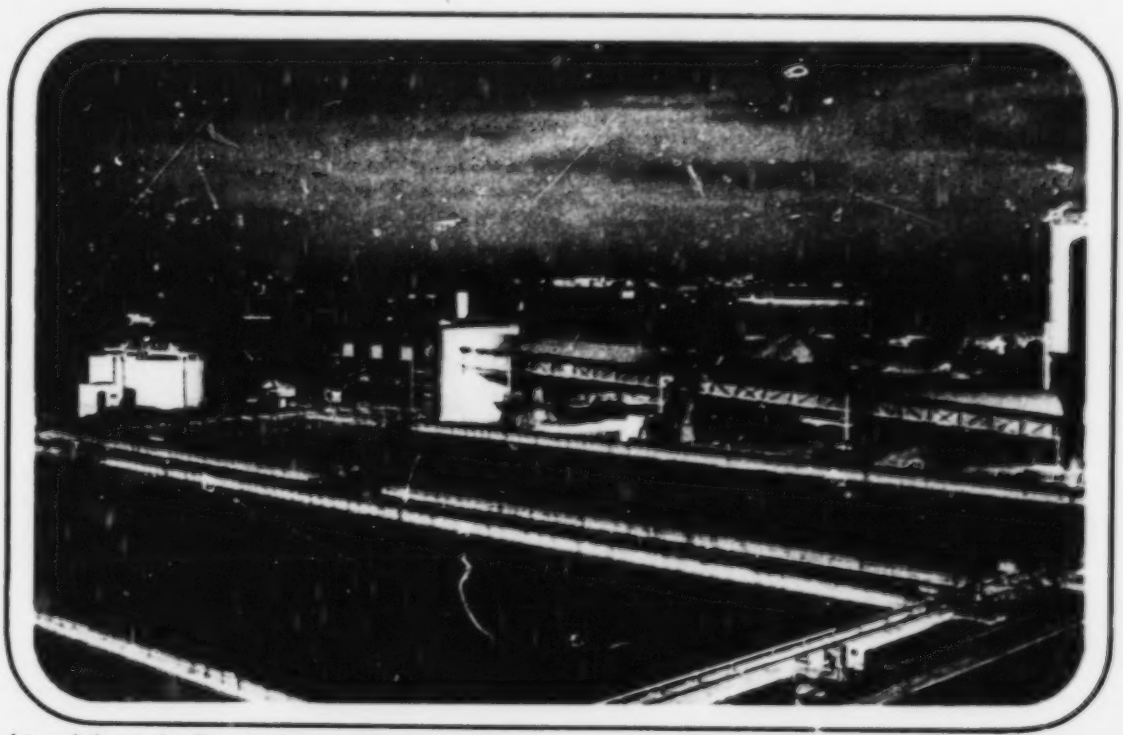
6. ENERGY CONSIDERATIONS

Since recalcination is an important unit process of the new technology, the initiation of a new procedure requiring approximately 9 million BTU/ton of quick-lime requires careful consideration. The following facts would appear to apply to all plants where recalcination would be used:

1. **Using commercial quicklime,** in larger tonnage than any other water treatment chemical, requires the following energy-consuming operations for its manufacture:
   a. Mining of limestone or marble in quarry.
   b. Transporting to kiln.
   c. Crushing and grinding before burning.
   d. Burning in vertical shaft or rotary kilns.
   e. Transporting in bulk shipment, frequently for hundreds of miles.
   f. Unloading and transporting to the water plant.



Interior of kiln



Lime kiln at the Dayton Water Treatment Plant

2. **Recalcining carbonated sludge would:**

   a. Eliminate a, b, c, e, and f above.

   b. Evaporate the moisture from the filter or centrifuge cake. The amount of heat required to do this is more than compensated for by the fact that recalcination produces more lime than is fed to the water.

   c. Produce more than sufficient CO_2 in the stack gas to carbonate the plant's finished water, for stabilization.

   d. Produce more than sufficient CO_2 to carbonate the plant sludge and make possible the recycling or recovery of the magnesium.

   e. Provide for recovery, in a heat exchanger, of the latent heat of evaporation of the sludge cake water. This is later used for recovering the $MgCO_3 \cdot 3\ H_2O$ and drying it.

   f. Decrease the cost of hauling sludge to disposal point.

The new process actually conserves energy and is a major factor in eliminating the sludge disposal problem.

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For Further
Information:

Detailed information on this project is available from the Superintendent of Documents as EPA Report 12120 HMZ "Plant Scale Studies of the Magnesium Carbonate Water Treatment Process."

Or write:

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